Remarks

The claimed invention requires *inter alia* a machine, where specifically claimed as a gas turbine engine, which has one or more internal components coated with a thermal barrier coating comprising a mixture of at least a refractory material and an indicator material having an optical emission spectrum which varies in response to a temperature of the respective component.

The Examiner is continuing to allege that the subject-matter of the independent claims (claims 20, 32, 35 and 47) is anticipated by and unpatentable over US-4560286 (Wickersheim). Wickersheim, however, makes no disclosure or suggestion of a thermal barrier coating as such is known to those skilled in the pertinent art.

As noted by the Examiner, Wickersheim does disclose (column 5, lines 39 to 46) the coating of a solid object (20) by a phosphor coating (40), where the phosphor is characterized by emitting, when excited, electro-magnetic radiation within separable bandwidths at two or more distinct wavelengths and with relative intensities in those bands that vary as a known function of the temperature of the phosphor (40). The Examiner is of the opinion that the phosphor coating (40) constitutes a thermal barrier coating as required by the claimed invention. This is absolutely not the case.

The term "thermal barrier coating" has a well-understood meaning in the art, such being a continuous coating over the surface of a component which has thermal insulating and structural properties that provide for protection of the underlying component at high temperatures, typically in gas turbine engines which experience very high temperatures, and typically at temperatures greater than 1000 °C, over extended periods of time, typically several thousand hours. In this regard, enclosed are extracts taken from publications from the relevant field of art, which clearly evidence that the term thermal barrier coating (TBC) has a clear and well-understood meaning. These extracts are provided as a small, representative sample from a very large number of publications which all provide the same teaching as to the meaning of the term thermal barrier coating.

Contrary to the Examiner's allegation, the applicants are not attempting to become their own lexicographer. Rather, applicants are construing the term thermal barrier coating in accordance with its well-understood meaning in the relevant field of art. This is consistent with applicants' specification, wherein it is clearly stated that the

present invention relates to thermal barrier coatings (page 1, line 2). In addition, applicants' specification points out on page 1, at lines 8-13:

> A thermal barrier coating typically comprises a relatively "thick" layer of a refractory or thermally insulating material such as yttria stabilised zirconia or YSZ. Here, the term "thick" is used to imply a thickness of, say, 250µm. The refractory material would generally be selected to have a low thermal conductivity such as around 1 to 3 W/mK, thereby reducing heat transfer to the components and reducing the temperature experienced by the components.

The phosphor coating (40) of Wickersheim is quite simply not a thermal barrier coating. Wickersheim discloses (column 7, lines 61 to 68) that the phosphor of the phosphor coating (40) is applied as a paint to the solid object (20). Such a painted phosphor is a coating, but manifestly not a thermal barrier coating.

In order to highlight the manifest dissimilarity between a phosphor paint coating and a thermal barrier coating, enclosed is a photographic summary, together with the actual samples, which contrasts the performance in a thermal environment of a simple, phosphor paint coating and a thermal barrier coating in accordance with the present invention.

In considering the teaching of Wickersheim, it is important to recognize that the teaching is to temperature measurement and not the provision of a thermal barrier coating. In being concerned only with temperature measurement, the phosphor coating (40) of Wickersheim does not have to possess any of the thermal insulating or structural properties of a thermal barrier coating.

The Examiner has also made reference to a teaching (column 6, line 68 to column 7, line 1) in Wickersheim regarding durability and stability, apparently considering this teaching to disclose that the coating material should be durable and stable. It is submitted that this referenced passage is being taken out of context. This passage actually states that "The phosphor material should also be durable, stable...", where this phosphor material is a component of the phosphor coating (40). Contrary to the Examiner's allegation, there is no disclosure to the durability or stability of the phosphor coating (40). Indeed, the disclosure to durability and stability is qualified as being "...capable of reproducing essentially the same results from batch to batch.", thus

clearly evidencing that the durability and stability is to the phosphor material and not the phosphor coating (40).

Accordingly, it is submitted that the claimed invention is clearly patentable over the disclosures of Wickersheim.

The Examiner is also continuing to allege that the subject-matter of the independent claims (claims 20, 32, 35 and 47) is anticipated by and unpatentable over US-5730528 (Allison et al.). This is not the case in that Allison et al. has nothing to do with a thermal barrier coating as such term is known to those skilled in the relevant art. Allison et al. makes no disclosure or suggestion of a thermal barrier coating, when such term is properly construed as above discussed.

As noted by the Examiner, Allison et al. discloses (column 5, lines 7 to 10 and lines 55 to 64) the provision of a coated phosphor pad (12) on an article (14), such as a component of a turbine engine, as clearly illustrated in Figure 1, for the purposes of enabling temperature measurement. This coated phosphor pad is, however, not a thermal barrier coating, where, as mentioned hereinabove and recognized in the relevant art, a thermal barrier coating is a continuous coating over the surface of a component which has thermal insulating and structural properties which provide for protection of the underlying component at high temperatures. A discrete phosphor pad, albeit formed by coating a discrete area on the article (14), is manifestly not a thermal barrier coating.

As regards the teaching of Allison et al., it is important to recognize that the teaching of Allison et al., similarly to that of Wickersheim, is to temperature measurement and not the provision of a thermal barrier coating as required by the claimed invention. Allison et al. makes no suggestion whatsoever as to the provision of a thermal barrier coating, in being motivated only by the provision of a phosphor pad for the purposes of enabling temperature measurement.

The entire teaching of Allison et al. is to the provision of a temperature-sensitive phosphor pad and the method of measuring temperature using the same (column 1, lines 11 to 15 and lines 52 to 54). This fact is clearly evidenced by the disclosure (column 4, lines 29 to 40) that the phosphor pad can be a coated pad, a single crystal pad or a sintered pad, where optionally fabricated to fit the underlying component. It is inconceivable that a person skilled in the art would have interpreted the teaching of
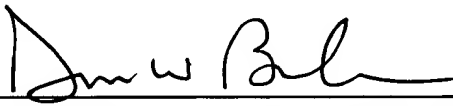
Allison et al. as to anything other than the provision of a discrete phosphor pad for the purposes of temperature measurement, and to allege otherwise would manifestly require an impermissible hindsight analysis of the prior art.

Accordingly, it is submitted that the claimed invention is clearly patentable over the disclosures of Allison et al.

In view of the foregoing, request is made for timely issuance of a notice of allowance. In the event the Examiner does not agree with the foregoing, the Examiner is requested to telephone the undersigned to arrange a time for an interview before issuing any further office action.

Respectfully submitted,

RENNER, OTTO, BOISSELLE & SKLAR, LLP

By _____

Don W. Bulson, Reg. No. 28,192

1621 Euclid Avenue, Nineteenth Floor
Cleveland, Ohio 44115
(216) 621-1113

Enclosures: "Performance of Phosphor Paint Coatings vs TBCS"
Harvey, "What is a thermal barrier coating (TBC)?"
Katz, "Advanced Ceramics: Thermal Barrier Coatings Beat the Heat"
Clarke et al., "Materials Design for the Next Generation Thermal Barrier Coatings"
Choi et al., "Delamination of multilayer thermal barrier coatings"
Levi, "Emerging materials and process for thermal barrier systems"
Wright et al., "Mechanisms governing the performance of thermal barrier coatings"
Takahashi et al. "Microstructural features of mechanical failure in thermal barrier coating systems under static loadings"
Eldridge et al. "Depth-Penetrating Temperature Measurements of Thermal Barrier Coatings Incorporating Thermographic Phosphors"
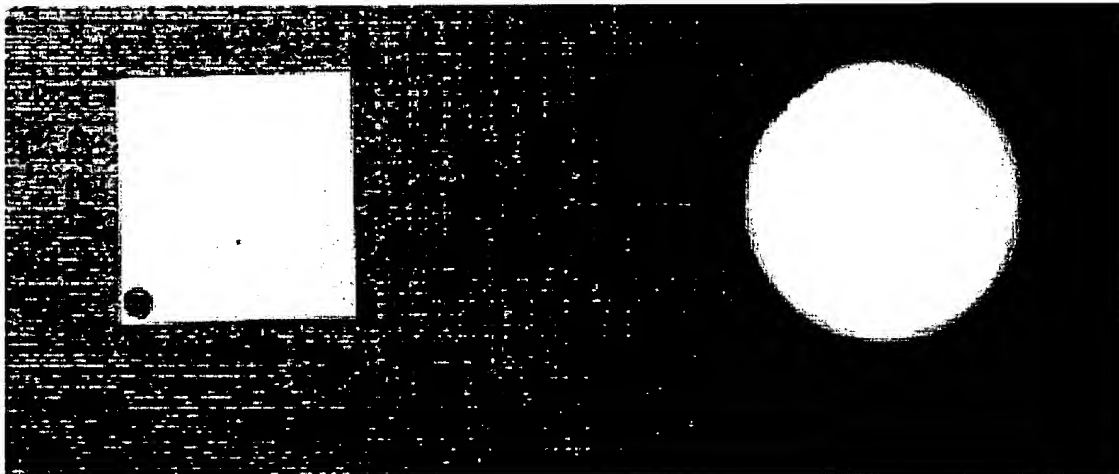
Z:\SEC152\152\DWB\FRYH\P\P0102\P0102US.R03.wpd

Page 5 of 5

PERFORMANCE OF PHOSPHOR PAINT COATINGS VS TBCS

For the purposes of comparison, samples of an object, here a metal substrate, coated both with a phosphor paint coating and a TBC have been prepared and subjected to thermal treatment.
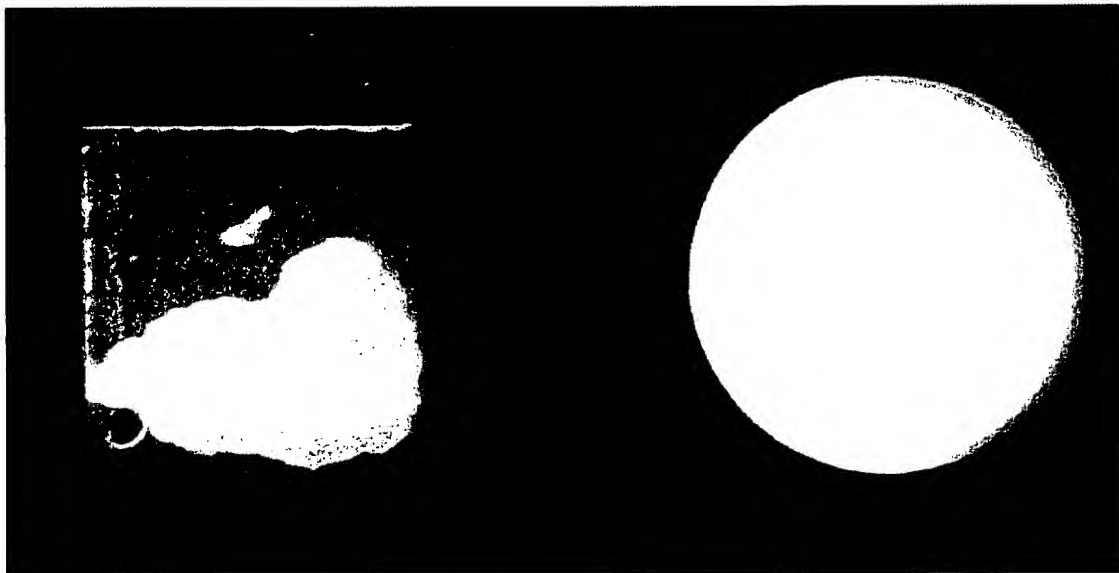
The square (left-hand) sample is a metal substrate coated with a phosphor paint coating. The circular (right-hand) sample is a metal substrate coated with a TBC which includes a luminescent indicator material in accordance with the present invention.

Before Heat Treatment

Prior to heat treatment, the phosphor paint coating and the TBC were visible as continuous (white) coatings, as shown in the above photograph.

After Heat Treatment

The sample coated with a phosphor paint coating was exposed to a limited thermal treatment, in being subjected three (3) times to a temperature of about 1100 °C, each of a one (1) minute duration. The damage to the coating is clearly visible in the above photograph. Some of the (white) coating remains, but a major part of the coating is no longer present, exposing the (dark) underlying metal substrate.

The sample coated with a TBC was exposed to a very much more severe thermal treatment, in being exposed five hundred (500) times to a temperature of about 1250 °C, each of a five (5) minute duration. The coating is undamaged, as represented by the continuous (white) coating in the above photograph.

TWI
TWI WORLD CENTRE FOR MATERIALS JOINING TECHNOLOGY

About TWI | Membership | Contact us | Industries | Technologies | Information & know-how |
Site map | *Join*IT® | Help

Search [   ] Go   Search Tips   Advanced search
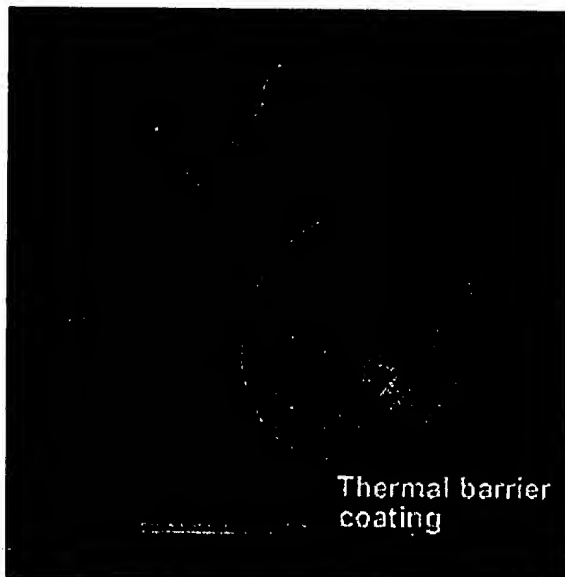
TWI Frequently asked questions

What is a thermal barrier coating (TBC)?

by Dave Harvey

Thermal barrier coatings (TBCs) perform the important function of insulating components, such as gas turbine and aeroengine parts, operating at elevated temperature. Typical examples are turbine blades, combustor cans, ducting and nozzle guide vanes. TBCs have made possible the increase in operating temperature of gas turbines.

TBCs are characterised by their very low thermal conductivity, the coating bearing a large temperature gradient when exposed to heat flow. The most commonly applied TBC material is yttria stabilized zirconia (YSZ) which exhibits resistance to thermal shock and thermal fatigue up to 1150°C. YSZ is generally deposited by plasma spraying and electron beam physical vapour deposition (EBPVD) processes. It can also be deposited by HVOF spraying for applications such as blade tip wear prevention, where the wear resistant properties of this material can also be used.

It is common practice to aluminise and pre-coat the substrate material (generally a nickel or cobalt superalloy) with an MCrAlY bond-coat. The bond-coat is necessary to accommodate residual stresses that might otherwise develop in the coating system, caused by the metallic substrate and the ceramic TBC having different coefficients of thermal expansion.

Gas turbine transition duct

Thermal barrier coating

Further information

What is an MCrAlY coating?
Surface engineering at TWI
Thermal spraying - high velocity oxyfuel (HVOF), arc and flame processes

Copyright © 2004, TWI Ltd

Link to related content, selected on the basis of keyword matches using the keyword set on the 'Advanced search' screen

TWI information

TWI

CONTENT

CI Home
About CI
Editorial Archives

IN THIS ISSUE

Current Features
Calendar of Events
Industry News
New Products
Classifieds

AD CONNECTIONS

Advertiser Index
Buyers' Connections
Company Profiles
Lit Showcases
Online Show Profile
Supplier Spotlights

RESOURCES

CI Giants
CI Giants Listing
Form
Data Book &
     Buyers' Guide
Equipment Digest
Materials Handbook
Refractories Review
Reference
Government Links
Industry Links
Trade Associations
NEW! Books
List Rental

SERVICES

Media Kit
Subscribe Online
Bulletin Board
Contact Us

All BNP Media

Want to use this article? CLICK HERE for options!

<< BACK | CERAMIC INDUSTRY HOME

Advanced Ceramics: Thermal Barrier Coatings Beat the Heat

By **R. Nathan Katz**

POSTED: 04/01/2001

If you've flown on a commercial jet aircraft recently, it's virtually certain that parts of its engine were protected by zirconia thermal barrier coatings (TBCs). These coatings are used to extend the life of metal components by creating a temperature drop across the coating, permitting the underlying metal to operate at a reduced temperature. Future gas turbines (GT) will use TBC technology to permit the simultaneous increase of turbine inlet temperature and the reduction of turbine cooling air, thereby increasing efficiency.

How TBCs Work

Superalloys used in GTs melt at temperatures between ~1200 and 1315°C. The combustion gases that flow through these engines are ~1350°C or higher. How do the engines run without melting? Large amounts of compressor air are used to cool the engine components, thereby avoiding melting, thermal fatigue and a variety of other potential failure modes. Providing this cooling air comes at the cost of decreasing engine performance and fuel economy. If less cooling air is required, fuel economy or other measures of performance can be increased. If cooling air and the temperature of the metal parts are simultaneously reduced, fuel economy and engine component lifetimes can be increased. This is what zirconia based TBCs do.

The properties of zirconia most critical for TBCs are a very low thermal conductivity (~1 W/mK) and a thermal expansion close to that of superalloys. If a thin layer of zirconia is coated on a cooled metal substrate, a significant DT can be supported across the layer. (If the substrate is not cooled, the DT will approach zero.) The zirconia coatings used in current engines can sustain a DT of ~165°C in airfoils, reduce specific fuel consumption by ~1%, increase thrust-to-weight ratios by ~5%, and significantly extend component life.

TBCs are a two-layer system composed of a zirconia layer ~0.254 mm thick, which faces the hot combustion gases, and an ~0.127 mm bond coat (typically, NiCoCrAlY alloy). The bond coat provides strong coating adherence and enhances the oxidation resistance of the substrate metals.

Applications

About 30 years ago TBCs of fully stabilized 22 wt % MgO/ZrO_2 were introduced

in the combustors of commercial aircraft. The coatings were applied by the plasma spray technique. In this process an electric arc ionizes an argon gas to form a plasma. Ceramic powders are injected into the plasma, heated to a "semiplastic" state, and accelerated toward the combustor surface. When the particles impact the target, a very complex interlocking microstructure, which is highly porous and microcracked, results. These coatings worked very well and extended combustor life as long as the temperature did not exceed ~980°C. Above this temperature, the MgO doped ZrO_2 destabilized and failed by spallation.

A second-generation material, 7 wt % yttria, partially stabilized zirconia (7YPSZ) is now in use, which provides a fourfold increase in coating life at temperatures of ~1090°C. A process for making denser TBCs with highly columnar structures has facilitated the insertion of zirconia based coatings onto blades and vanes. This process, electron beam-physical vapor deposition (EB-PVD), relies on vaporizing the 7YPSZ with an electron beam and positioning the part so that the vapor will deposit where desired. Using this process, highly columnar grains of 7YPSZ have been deposited on airfoils. The columnar structure provides interfaces that are weakly bonded and thus separate at low stresses. This provides a coating with a high strain and thermal cycling tolerance. Airfoils with such coatings have been in airline service since the late 1980s.

Future Directions

EB-PVD TBCs have a thermal conductivity of ~1.8 W/mK, compared to ~1 W/mK for plasma sprayed coatings. One way of achieving a lower value of conductivity in the EB-PVD zirconia is to process it in a way that yields a multilayer substructure within each columnar grain. Such work is being actively pursued. Alternative materials under study include lanthanum phosphate and lanthanum hexaaluminate. The latter material may be useful in the 1100-1600°C range.

For Further Reading

1. T. Abraham, "A Cutting Edge in High-Performance Ceramic Coatings," *Ceramic Bulletin,* March 1999 pp. 69-71.
2. S M Meier, D K Gupta, and K D. Sheffler, "Ceramic Thermal Barrier Coatings for Commercial Gas Turbine Engines," *J. of Metals,* March 1991, pp. 50-53.
3. S M Meier and D K Gupta, "The Evolution of Thermal Barrier Coatings in Gas Turbine Engine Applications," *Trans. of the ASME,* vol. 116, January 1994, pp. 250-256.
4. J Kumpfert, M Peters, and W A Kayser, "Advanced Materials and Coatings for Future Gas Turbine Technology," in the Proceedings of the NATO-RTO Symposium on, *Gas Turbine Operation and Technology for Land, Sea and Air Propulsion and Power Systems,"* Ottawa, Canada, October 18-21, 1999.

ABOUT THE AUTHOR:

R. Nathan Katz is the Norton Research Professor in the Department of Mechanical Engineering at Worcester Polytechnic Institute, Worcester, MA. He is also a Fellow of the American Ceramic Society.

Related Features

- A Grain of Niobium:
  Additives for the Ferrite Industry
- Raw and Manufactured Materials for Ceramics: 2001 Overview
- Oglebay Norton Seeks To Re-Incorporate In Ohio To Save Taxes
- Executive Overview: Business Watch (Advanced Ceramics)
- Advanced Ceramics: NTC Thermistors
- Investing In Ceramics: Ferro Moves Forward in the Electronic Materials Market
- Advanced Ceramics: Ceramic Filters and Membranes

- New Ceramics for Wireless Applications
- Copper End Terminations for BME Capacitors
- Investing In Ceramics - Growing with Demand
- Materials: Synthesizing Cordierite in Ceramic Bodies
- Advanced Ceramics: Nuclear Ceramics: A Renaissance?
- Growth Prediction Lowered for U.S. Advanced Ceramics Industry
- A Binding Matter
- Achieving Self-Glazed Porcelain Bodies
- A Fine Solution For Advanced Applications
- Investing in Ceramics: Abrasives Merger Secures Domestic SiC Source
- Investing in Ceramics: Advanced Industries International Celebrates First Birthday
- Advanced Ceramics: Zeolites = More Miles Per Barrel
- Advances in Sol-Gel Technology
- Optimizing Enamel Adhesion
- Exploring the Nanoparticle Potential
- Inside CI: Sometimes Good Things Start Small
- ONLINE EXCLUSIVE - Behind the Scenes: Jack McMahon, President of PEMCO Corp.
- ONLINE EXCLUSIVE - Association Update: The Porcelain Enamel Institute
- Investing in Ceramics: When Opportunity Knocks
- ONLINE EXCLUSIVE: Commercializing Nanomaterials
- ONLINE EXCLUSIVE: Emerging Opportunities for Carbon Nanotubes
- Advanced Ceramics—It's All in the Polymer
- Raw & Manufactured Materials: 2002 Review & Forecast
- Investing In Ceramics: Manufacturing for Quality
- A Refractory Coating From Outer Space
- Advances in Porcelain Enameling
- Plasma Sprayed Ceramic Coatings
- Investing in Ceramics: Advancing Technical Ceramics
- Improving Electronic Ceramics with Niobium and Tantalum
- Ceramic Opportunities in Fuel Cells
- Grinding Cermet Tool Materials
- High-Performance Insulation for Hydrogen Sintering
- Murata Names Denslinger Executive V.P. Of Sales And Marketing

ONLINE click here...

A **bnp** WEBSITE

MATERIALS DESIGN FOR THE NEXT GENERATION THERMAL BARRIER COATINGS

D.R. Clarke and C.G. Levi

Materials Department, College of Engineering, University of California, Santa Barbara, California 93106-5050; email: clarke@engineering.ucsb.edu

Key Words   zirconia, materials science, high temperature

■ **Abstract**   The emphasis in this short review is to describe the materials issues involved in the development of present thermal barrier coatings and the advances necessary for the next generation, higher temperature capability coatings.

INTRODUCTION

The development of today's gas turbine engines has been the result of continual improvements in a wide variety of engineering skills including turbine design, combustion, and materials. One measure of the substantial improvements over the past five decades is the increase in the maximum gas temperature at a turbine airfoil afforded by these improvements, as shown in Figure 1. The increase in airfoil temperature has been facilitated by three principal materials developments: dramatic advances in alloy design to produce alloy compositions that are both more creep resistant and oxidation resistant; advances in casting technology that have facilitated not only the casting of large single-crystal superalloy blades and vanes but also the intricate internal channels in the blades to facilitate cooling; and the development of a viable coating technology to deposit a conformal, thermally insulating coating on turbine components. The advances and developments in the first two areas have been reviewed extensively elsewhere (1). Less well known is the development of thermal barrier coatings (TBCs), even though in the last decade their use has enabled a dramatic increase in airfoil temperature, far greater than that enabled by the switch from cast alloy blades to single crystal blades over approximately 30 years.

As originally envisaged, the primary function of a TBC is to provide a low thermal conductivity barrier to heat transfer from the hot gas in the engine to the surface of the coated alloy component, whether in the combustor or the turbine (Figure 2). The TBC allows the turbine designer to increase the gas temperature, and thereby the engine efficiency, without increasing the surface temperature of the alloy. Subsequently, it has been recognized that a TBC also confers additional benefits, for instance, providing protection to rapid thermal transients such as occur
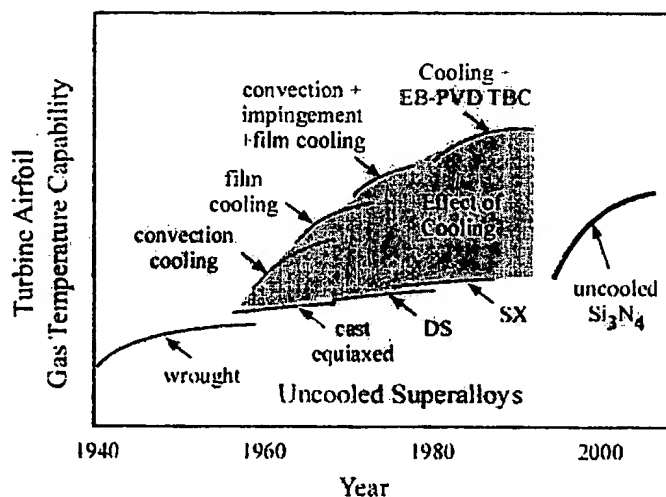
383

Figure 1 Increase in turbine airfoil temperature over the last six decades through combinations of materials advances and associated developments in cooling techniques. Since this diagram was constructed, the shaded region has extended to the present year, and the use of uncooled silicon nitride remains for the future.

due to flame out, and as a means to even out local temperature gradients. Indeed, in some cases, the use of a TBC has simplified the design of blades by minimizing thermal distortions of the blade. However, undoubtedly the biggest benefit of TBCs has been to extend the life of alloy components in the hottest sections in an engine by decreasing their surface temperatures.

Present day TBCs generally consist of a yttria-stabilized zirconia (YSZ) coating deposited onto an oxidation-resistant bond-coat alloy that is first applied to a nickel-based superalloy component (Figure 2). In diesel engine applications where the temperatures are usually lower, the YSZ coating is generally applied directly onto the alloy. Two main types of coating are in use. For relatively small components such as blades and vanes in aerospace turbines, the coatings can be applied by electron-beam physical vapor deposition (EB-PVD). For larger components such as the combustion chambers and the blades and vanes of power generation, stationary turbines, the coatings are usually applied by plasma-spraying (PS). In many respects, the choice of materials and their production represent a mature materials technology. While improvements in their capabilities continue, there is a growing realization that new TBC systems will be required for the next generation turbines presently being designed. To set the stage for coming developments, we first review the selection of materials used in present YSZ coatings, some of the new insights that have been gained in understanding how YSZ coatings
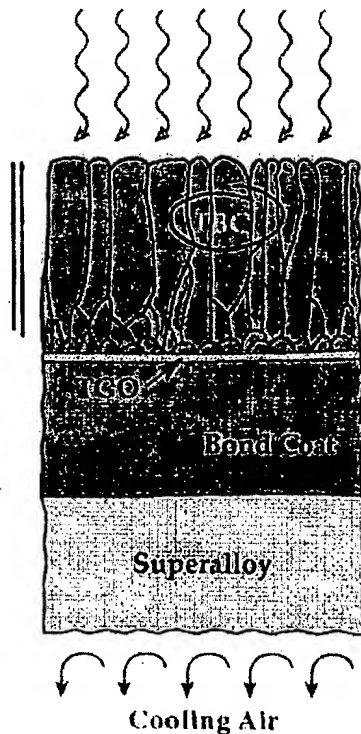
Figure 2   Schematic illustration of a TBC and the associated bond-coat on a superalloy in a thermal gradient.

fail, and then describe approaches to the development of the next generation TBC systems.

PRINCIPAL REQUIREMENTS OF A THERMAL BARRIER COATING

The turbine designers' primary requirement of a TBC is that it have a low thermal conductivity and, for rotating components, preferably also a low density to minimize centrifugal loads. At the materials design level this translates into three additional requirements. First, the material must have strain compliance so as to withstand the strains associated with thermal expansion mismatch between the coating and the underlying alloy on thermal cycling. The use cycle, both the maximum temperature and the times at temperature, of course, varies between aircraft and power generation turbines, but nevertheless the coating must accommodate the large strains associated with thermal cycling. The need for strain compliance is illustrated in Figure 3, where the thermal expansion coefficients of zirconia,

Delamination of multilayer thermal barrier coatings

Sung Ryul Choi [a], John W. Hutchinson [b,*], A.G. Evans [b]

[a] *Department of Mechanical Engineering, Yeungnam University, Kyongsan 712-749, South Korea*
[b] *Division of Engineering and Applied Sciences, Harvard University, Pierce Hall, Cambridge, MA 02138, USA*

Received 11 September 1998; received in revised form 9 March 1999

Abstract

Multilayer thermal barrier coatings (TBCs) on superalloy substrates are comprised of an intermetallic bond coat, a thermally grown oxide (TGO) layer, and a porous zirconia top coat that provides thermal protection. The TGO attains a thickness of 1–10 μm prior to failure, while the bond coat and zirconia layer are each about 50–100 μm thick. The preferred method for manufacturing TBCs comprises electron beam deposition. This method produces a thin "fully dense" zirconia layer 1 μm or 2 μm thick between the TGO and the thick "top coat". Edge-delamination and buckling-delamination are the expected failure mechanisms. Each is addressed. Both occur at the interface between the bond coat and the TGO. Since low in-plane elastic moduli of the porous zirconia layer promote the latter, but suppress the former, there exists a range of moduli wherein both types of failure can be avoided. Two distinct sizes govern buckling-delaminations. Small scale delaminations arise when the TBC top coat has a very low modulus. They have a characteristic size that scales with the thickness of the TGO plus the fully dense zirconia layer: typically tens of microns. In this domain, the dense TGO/ZrO₂ bi-layer buckles by pushing into the thick, more compliant zirconia top layer. The larger scale delaminations occur when the top coat is stiff. They involve not only the bi-layer, but also the zirconia top layer; buckling away from the substrate as a tri-layer. In this case, the total thickness of the TBC determines the extent of the delamination, typically several 100 μm. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Thermal barrier coatings (TBCs) consisting of stabilized zirconia are now employed in most turbine engines, permitting gas temperatures to be raised substantially above those for uncoated systems. A detailed description can be found in a recent National Research Council Report (Hillery, 1996). High temperatures are enabled by the low thermal conductivity of the zirconia TBC, coupled with active cooling of the underlying metal. TBC systems are multilayered. They are designed to inhibit oxidation of the substrate by means of an intermetallic bond coat, as well as provide thermal protection through the TBC itself. The coatings must be able to withstand the mismatch strains generated each time the engine is thermally cycled. TBC durability relies on the integrity of the interfaces: that located between layers as well as that with the substrate. Delamination and spalling are the most common failure modes (DeMasi-Marcin et al., 1989; Lee and Sisson, 1994; Christensen et al., 1996; Sergo and Clarke, 1998; Wang and Evans, 1998; He et al., 1998; Wang and Evans, 1999).

* Corresponding author. Tel.: +1 617 495 2848; fax: +1 617 495 9837; e-mail: hutchinson@husm.harvard.edu
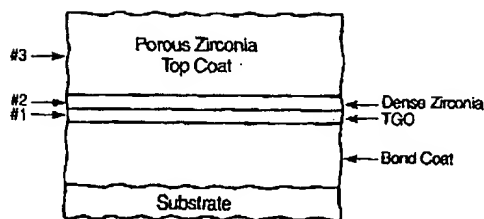
Fig. 1. Layered structure of TBCs considered in this paper.

The layered structure of a representative TBC is shown in Fig. 1. A Ni-based bond coat containing Al, Cr, Co and Y is applied to the superalloy substrate prior to deposition of the zirconia. Upon exposure at operational temperatures, a thermally grown oxide layer (TGO) forms between the bond layer and the zirconia. The TGO (usually Al_2O_3) provides the oxidation protection. It is typically in the range 1–10 μm when the TBC spalls. Advanced TBCs are made by electron beam deposition (Hillery, 1996). Coatings made by this method have a dense layer of zirconia just above the TGO, with thickness one or two microns. Above this dense layer is a relatively thick porous zirconia layer (50–100 μm), the so-called "top coat", which provides the thermal insulation. The columnar grains in this layer have gaps between them that provide in-plane moduli over an order of magnitude smaller than those found for dense ZrO_2 (Johnson et al., 1995). [1] Low moduli are essential to the survival of the TBC as will be explained shortly. Deposition of the zirconia and formation of the TGO both occur at high temperature (≈1100°C). Accordingly, because the coefficients of thermal expansion of the ceramic layers $(\alpha_1, \alpha_2, \alpha_3)$ are considerably smaller than that of the alloy substrate (α_s), they are subject to in-plane compressive strains in each cooling cycle (stresses on the order of a GPa or more in the TGO and the fully dense zirconia layer (Christensen et al., 1997).

Delamination at the interface between the TGO and the bond coat, with subsequent spalling, is the

chief failure mechanisms for electron beam deposited TBCs (DeMasi-Marcin et al., 1989; Sergo and Clarke, 1998). The failure initiates as an interface separation, which grows by thermomechanical fatigue, accompanied by thickening of the TGO. When the separations become large enough, either large scale buckling or edge delamination are activated. Buckles and delaminations subsequently lead to spalling, wherein the interface crack deflects through the TGO and the TBC up to the free surface (Wang and Evans, 1998; Sergo and Clarke, 1998). The failure is driven primarily by the high compressive stresses in the TGO (Christensen et al., 1996).

Edge-delamination is probable when the in-plane moduli of the thick top coat are moderately high, caused by the large elastic strain energy which develops during cooling. For example, a fully dense 100 μm zirconia top coat would develop a compressive stress of approximately 1 GPa and an elastic energy per unit area of $250 \ J \ m^{-2}$. This energy density far exceeds the toughness of the interface between the TGO and the bond coat (Wang and Evans, 1998; Sergo and Clarke, 1998), making it virtually certain that the TBC would delaminate (starting either at an edge or from a region of high substrate curvature). On the other hand, high in-plane moduli of the top coat make the TBC less susceptible to buckling at small initial debonds or interface flaws, and therefore can have a beneficial influence in suppressing buckling-delamination. Conditions for buckling-delamination of a multilayer coating will be derived in this paper. *Quantitative models for the two competing delamination mechanisms will be employed to estimate the range of in-plane moduli where both mechanisms can be suppressed.*

A synopsis of relevant results from the literature for delamination of single layer films will be given in Section 2, serving as background to the present study. Two size domains characterise buckling-delamination of multilayers. One of these refers to large scale buckles (LSB), wherein the buckle length appreciably exceeds the overall multilayer thickness. The analysis of this domain, presented in Section 3, is applicable to any multilayer. The second domain, addressed in Section 4, operates when the top layer has low in-plane moduli, as is

---

[1] The low modulus reflects the alignment and morphology of the porosity.

Emerging materials and processes for thermal barrier systems

Carlos G. Levi *

Materials Department, University of California, Santa Barbara, CA 93106-5050, USA

Accepted 23 March 2004

Abstract

Thermal barrier systems have been the subject of vigorous research and development activities over the past few years, driven by the demands for enhanced reliability and substantially higher operating temperatures envisaged for the next generations of gas turbine engines. The menu of candidate materials and architectures has expanded considerably, including numerous concepts based on zirconia as well as radically different materials, multilayers and modulated distributions of porosity and chemical composition. Advances in deposition processes enable increased flexibility for tailoring composition and microstructure to local requirements within the coating system, e.g. for thermal insulation, control of interdiffusion, enhanced resistance against environmental degradation and condition monitoring. Many challenges remain but healthy and growing collaborations between the science and technology communities bode well for future progress in this area.
© 2004 Elsevier Ltd. All rights reserved.

1. Introduction

The past decade has seen the emergence of engineered coating systems as arguably *the* crucial materials problem for the next generation of gas turbine engines [1]. First adopted simply as a means to enhance the durability of metallic components in the hostile engine environment, coatings are now envisaged as prime-reliant elements in design, essential to extend the performance limits of current alloys as well as to enable the utilization of ceramics in gas turbines. Specifically, thermal barrier coatings (TBCs) offer a quantum leap in temperature capability equivalent to three decades of progress in alloy design, processing and cooling engineering [2], but reliability concerns have largely limited their use to reducing the effective temperature of the metallic component and thus extending its life [3]. Current engine design goals, however, are unlikely to be met unless major advances are made in both coating reliability *and* performance. Moreover, candidates to replace superalloys in the longer term, e.g. refractory silicides and ceramics, are now acknowledged to require both thermal and environmental barriers for their implementation [4,5]. Recognition of the latter need is rather recent, motivated by engine tests [6,7] that

brought into light the full magnitude of the moisture attack problem on silicon-based ceramics [8]. The result of these trends has been a marked increase in TBC research activity, with approximately half of the total number of publications over the last 30 years [1] appearing after the last Current Opinion review on this subject [9].

A substantial number of reviews on various aspects of TBCs are found in the recent literature, e.g. [10–16]. In combination, they reflect a field evolving from a successful technology built largely on a heuristic foundation, with a small menu of materials and largely preoccupied with reliability, to an increased emphasis on the scientific understanding of the dynamics of these systems, the development of mechanism-based models and the diversification of materials to address the performance and durability demands of new generations of engines. In an effort to complement recent reviews and minimize overlap, this paper focuses on materials and process developments primarily aimed at enhancing performance, with selected comments on relevant durability issues. The emphasis is on the thermal barrier (Fig. 1) because it represents the area with greater diversity of alternate material concepts emerging in the period under review (not surprisingly since current

---

* Tel.: +1-805-893-2381; fax: +1-805-893-8486.
  E-mail address: levic@engineering.ucsb.edu (C.G. Levi).

[1] Based on a SciFinder Scholar search for references under the topic "thermal barrier coatings".
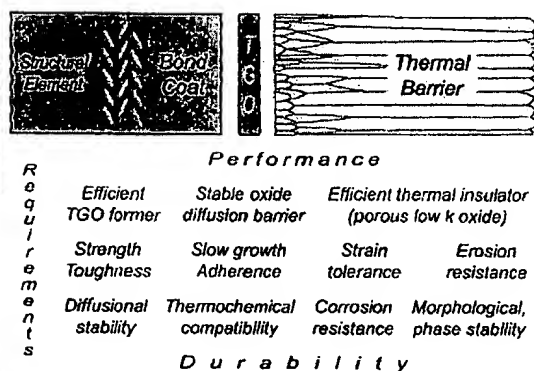
technology is based essentially on a single material). Selected developments in bond coats are briefly reviewed but justice cannot be done to the importance of the subject within the scope of this paper. The reader is referred to [14] for a recent and more extensive review on bond coats.

2. The thermal barrier system

The generic constituents of a thermal barrier system for a superalloy component are illustrated in Fig. 1, along with a summary of requisite attributes for performance and durability. The baseline thermal barrier or "top coat" is a 125–250 μm layer of porous ZrO_2 partially stabilized with 7 ± 1 wt.% Y_2O_3 (7YSZ), applied by either air-plasma spray (APS) or electron-beam physical vapor deposition (EB-PVD). Environmental protection relies primarily on a thin (<10 μm), dense Al_2O_3 layer (TGO), grown during service by thermal oxidation of the underlying metal. (Concepts for additional environmental barriers exist, e.g. for protection against the attack of molten deposits, but none has become part of the baseline system so far.) Because superalloys are optimized for mechanical performance, their surfaces must be modified chemically to promote the formation of a stable, adherent TGO. These modified surfaces or "bond coats" (BCs) are classified into two major groups: (i) single phase β-(Ni,Pt)Al (B2), applied by electrodeposition of Pt and subsequent aluminizing by some form of chemical vapor deposition (CVD) with concurrent interdiffusion, and (ii) overlay two-phase $(\gamma' + \beta/\gamma)$ MCrAlY's, applied by low pressure plasma spray (LPPS) or by EB-PVD [14].

The most important development at the system level has been the emergence of a "systems perspective" [11], wherein functionality may be viewed as depending primarily on the attributes of the individual layers, whereas durability is usually dominated by their interplay. Consequently, modeling has taken an increasingly prominent role not only as a tool for elucidating the underlying mechanisms but, more importantly, as the only viable approach to integrate the contributions of the multiplicity of complex phenomena occurring within the system. TGO growth and the associated evolution of stresses, damage and eventually spallation of the top coat upon thermal cycling continue to be the primary focus of the durability models [17–21]. Increased sophistication in the models has captured some of the effects of the neighboring layers on the critical TGO dynamics, e.g. [20,22,23] but the experimental evidence indicates that much remains to be done in this area. A notable example of the interaction between modeling and experimental work during this period relates to the development of displacement instabilities in the TGO [24] whose origin has been a subject of considerable debate and remains unresolved. Proposed contributions arise from cyclic plasticity in the BC and TGO [25,26], phase transformations in the bond coat [27,28], and the in-plane growth strain in the TGO [24]. The mechanism responsible for the latter has also been a subject of considerable interest and discussion during the review period [29].

3. Advances in thermal barrier materials and processes

Current technology is based essentially on one thermal barrier material, 7YSZ. The selection of this composition and its continued preference is a prime example of the predominance of durability over performance. Higher Y contents offer improved insulating potential [30,31] but 7YSZ showed superior cyclic life in early tests [32] and continues to prevail over novel materials based on similar criteria and its established processability by both APS and EB-PVD. While it is generally acknowledged that 7YSZ is yet to be utilized to its full potential, the search for alternate materials has intensified in the recent past, predicated primarily on the prospect of substantially higher operating temperatures. At issue are the ageing effects on the phase stability of 7YSZ above ~1200 °C [33,34], as well as on the pore content and architecture needed to achieve strain tolerance [35,36] and desirable reductions in the thermal conductivity (κ) [37,38]. There is also a growing concern about various forms of attack associated with contaminants in the gas stream, including erosion [39–41], foreign object damage [42], loss of compliance by penetration of molten deposits [43,44], and de-stabilization by hot corrosion [45–47].

Much of the research on thermal barrier materials has been driven by the desirability of further reducing κ and improving microstructure stability at high temperature. The approaches taken can be broadly classified as

Mechanisms governing the performance of thermal barrier coatings

P.K. Wright[a,*], A.G. Evans[b,c]

[a]GE Aircraft Engines,1 Neumann Way, G50, Cincinnati, OH 45215, USA
[b]Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA
[c]Princeton University, Princeton, NJ 08540, USA

Abstract

Thermal barrier coatings (TBCs) are now used on hot section components in most commercial turbine engines. They are used to enhance the temperature differential between the gas and the underlying metal surfaces. They comprise several layers designed to simultaneously provide thermal and oxidation protection. They have microstructures which afford sufficient strain tolerance that they remain attached despite severe thermomechanical cycling. Eventually, they spall. This happens because a thin, highly stressed, thermally grown oxide (TGO) develops beneath the TBC. In this article, the specific mechanisms that contribute to failure are described, with the motivation that this understanding can be used to design TBCs having greater reliability and durability. © 1999 Published by Elsevier Science Ltd. All rights reserved.

1. The thermal barrier system

Thermal barrier coatings (TBCs) comprise thermally insulating materials having sufficient thickness and durability that they can sustain an appreciable temperature difference (up to 100°C) between the load bearing alloy and the coating surface [1,2]. The benefits of these coatings result from their ability to sustain high thermal gradients in the presence of adequate back-side cooling. Lowering the temperature of the metal substrate surface prolongs the life of the component, whether from environmental attack, creep rupture, or fatigue. In addition, the coating reduces the thermal gradients in the metal substrate, reducing the driving force for thermal fatigue. Both of these benefits can be traded off in design for either greater component durability, or for reduced cooling air or higher gas temperature and improved system efficiency. As a result, these coatings have been increasingly used in turbine engines [3]. Successful implementation has been realized using comprehensive testing protocols to specify performance domains, facilitated by engineering models [4–7]. Expanded application to more demanding scenarios requires that their basic thermomechanical characteristics be understood and quantified, including the associated failure mechanisms. This need provides the opportunities and challenges discussed in this article.

There are *four primary elements* in a thermal protection system. They comprise: (i) the TBC itself; (ii) the super-

alloy substrate; (iii) an aluminum-containing bond coat (BC) between the substrate and the TBC; and (iv) a thermally grown oxide (TGO), typically alumina, that forms between the TBC and the BC (Fig. 1) [8]. The TBC is the insulator, the BC provides the oxidation protection and the alloy sustains the structural loads. The TGO is a reaction product. Each of these elements is dynamic and all interact to control the performance and durability. TBC design requires that these elements be well delineated, subject to the following particularly critical factors.

The TBC itself must be 'strain tolerant' to avoid instantaneous delamination. This is achieved by incorporating either microcracks or aligned porosity [3,9]. Two methods are used to deposit such TBCs. One uses electron beams to evaporate the oxide from an ingot and directs the vapor onto the preheated component [9]. It is designated electron beam physical vapor deposition (EBPVD). The deposition conditions are designed to create a columnar grain structure with both intra- and inter-columnar porosities that, respectively, enhance the thermal resistance and control the strain tolerance. The second method comprises plasma spray (PS) deposition, with conditions designed to incorporate intersplat porosity that serves both functions [10].

Zirconia has emerged as the preferred TBC, stabilized into its cubic form by the addition of yttria in solid solution. This material has low thermal conductivity (about 1 W/m² K) with minimal temperature sensitivity [11]. This desirable thermal behavior is attributed to the influence of the yttria in solution on the phonon scattering. Among the

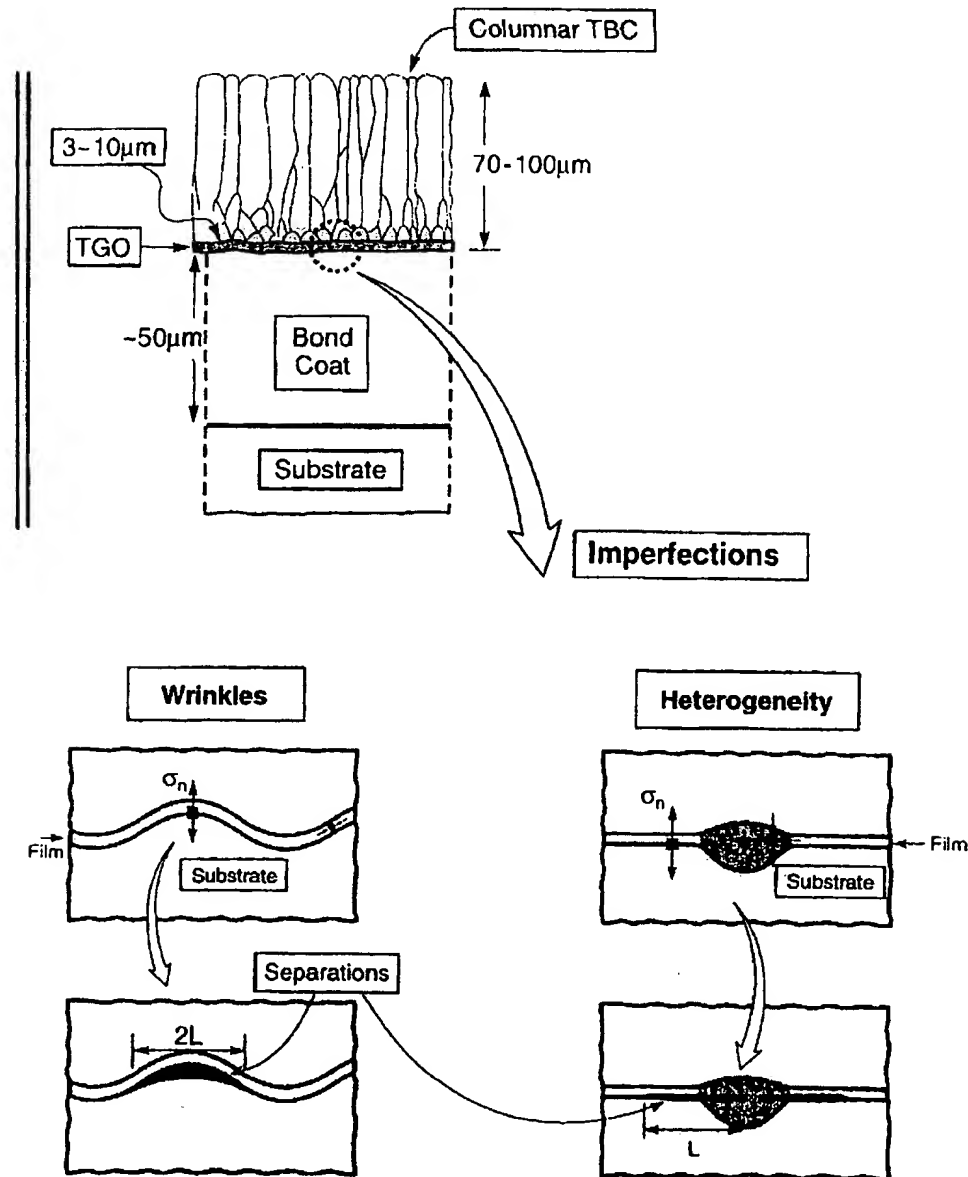---

*Corresponding author. Tel.: +1-513-243-8334.

Fig. 1. Schematic cross-section of thermal barrier system showing the thermal barrier coating (TBC), the Al-containing bond coat (BC), the thermally grown oxide (TGO) and the substrate. Also shown are two of the TGO imperfections that nucleate the failure process.

binary oxides, only CeO has a (slightly) lower thermal conductivity [11]. Various proposals have been made for ternary and quaternary oxides having even lower conduction, but there has been no experimental affirmation [12]. Porosity introduced during deposition enhances the intrinsic thermal resistance. This function is served in EBPVD coatings by intra-columnar porosity and in PS coatings by the intersplat porosity.

2. Durability issues

Growth of the TGO is a dominant phenomenon controlling durability [14]. The bond coat alloy comprises a relatively large local Al reservoir, such that alumina forms in preference to other oxides. The preference for alumina relates to its low growth rate and superior adherence. The TGO forms because the TBC allows ready ingress of

Microstructural features of mechanical failure in thermal barrier coating systems under static loadings[†]

S. Takahashi[1], M. Yoshiba[1] and Y. Harada[2]

[1]Department of Mechanical Engineering, Graduate School of Engineering, Tokyo Metropolitan University, Tokyo 192-0397, Japan

[2]Thermal Spraying Technology R & D Laboratory, Tocalo Co. Ltd, Kobe 658-0013, Japan

In order to clarify qualitatively and quantitatively the failure mechanism of plasma-sprayed thermal barrier coating (TBC) systems from the microstructural viewpoint, in situ observation of the mechanical failure behavior was conducted for TBC systems under the static loadings at ambient temperature; as the most fundamental aspect, by means of an optical microscopy. Several kinds of TBC systems were prepared by using different sorts of ceramic coating materials. Mechanical tensile loading or compressive loading was gradually applied to the plate shape of TBC specimen using a four-point bending test methodology. It was found that the tensile failure behavior of TBC systems depends strongly on the top-coat microstructures as well as heat treatment after the plasma spraying. The compressive failures were also found rather incidental and depended on the strength of top-coat at the interfacial region. Among different TBC systems, those with the finely segmented top-coat exhibited a good spalling resistance.

1. INTRODUCTION

Thermal barrier coatings (TBCs) are applied extensively to the critical hot section components of advanced heat engines such as nozzle guide vane, buckets and combustion chambers of gas turbines, to improve thermodynamic efficiency [1,2]. In order to increase the thermal efficiency of such the advanced land-based gas turbines, an increase in the operating temperature is most effective, but it means that the gas turbine components with TBC systems must endure to the very severe thermal-mechanical loadings [3,4]. Under service operating condition, in particular, the temperature–strain cycle experienced in the blade is much complicated and is different depending on the portion of the blade [5–7]. For example, the maximum tensile strain occurs at higher temperature on the pressure surface, while it is rather significant at lower temperature regime on the leading edge. Therefore, it is essential for the successful application of TBC systems that the mechanical failure mechanisms are well understood not only under high temperature condition but also under lower temperatures.

The failure mechanism for TBC systems under mechanical loading has been hardly clarified, although

numbers of studies have made about the failure mechanism under thermal loading [8,9].

In the present study, in situ observation of the mechanical failure behavior under the static tensile or compressive loading was conducted for the plasma sprayed TBC systems by means of an optical microscopy at ambient temperature; as the most fundamental aspect to be clarified. Several kinds of TBC systems were prepared with different coating parameters. The TBCs failure was quantitatively evaluated in relation with the mechanical strain applied to the ceramic top-coat. Namely, an influence of the microstructure in TBCs on the crack initiation and propagation behavior was investigated in detail.

2. EXPERIMENTAL

2.1 TBC systems

Several kinds of TBC systems, which are commonly composed of the ceramic top-coat/metallic bond-coat/ nickel-base superalloy substrate, were adopted in this study. TBC systems and their processing conditions are summarized in Table 1. Precipitation-strengthened nickel-base superalloy René 80 was used for alloy substrate with specimen geometry of 60mm length, 10mm width and 3mm thickness. Specimen surface was grit-blasted, cleaned and then low-pressure plasma sprayed (VPS) with CoNiCrAlY (Co-32Ni-21Cr-8Al-

Depth-Penetrating Temperature Measurements of Thermal Barrier Coatings Incorporating Thermographic Phosphors

Jeffrey I. Eldridge, Timothy J. Bencic, Stephen W. Allison, and David L. Beshears

Thermographic phosphors have been previously demonstrated to provide effective non-contact, emissivity-independent surface temperature measurements. Due to the translucent nature of thermal barrier coatings (TBCs), thermographic-phosphor-based temperature measurements can be extended beyond the surface to provide depth-selective temperature measurements by incorporating the thermographic phosphor layer at the depth where the temperature measurement is desired. In this paper, thermographic phosphor (Y_2O_3:Eu) fluorescence decay time measurements are demonstrated to provide through-the-coating-thickness temperature readings up to 1100 °C with the phosphor layer residing beneath a 100-μm-thick TBC (plasma-sprayed 8 wt.% yttria-stabilized zirconia). With an appropriately chosen excitation wavelength and detection configuration, it is shown that sufficient phosphor emission is generated to provide effective temperature measurements, despite the attenuation of both the excitation and emission intensities by the overlying TBC. This depth-penetrating temperature measurement capability should prove particularly useful for TBC diagnostics where a large thermal gradient is typically present across the TBC thickness. The fluorescence decay from the Y_2O_3:Eu layer exhibited both an initial short-term exponential rise and a longer-term exponential decay. The rise time constant was demonstrated to provide better temperature indication below 500 °C while the decay time constant was a better indicator at higher temperatures.

---

1. Introduction

Thermal barrier coatings (TBCs) provide highly beneficial thermal protection for turbine engine components.[1] TBCs are ceramic oxide coatings with low thermal conductivity; the most widely used TBC for turbine engine applications is composed of 8 wt.% yttria-stabilized zirconia (8YSZ). The measurement of temperature gradients through the TBC is critical for the evaluation of TBC performance and health monitoring as well as for the accurate simulation of thermal gradients in engine environments. Non-contact surface temperature measurements of translucent TBCs in a flame environment have proven difficult.[2] One problem with the application of infrared (IR) pyrometry to TBCs in an engine environment is that in addition to the thermal radiation emitted by the TBC, the pyrometer will also measure the radiation from the hot environment that reflects off the TBC and therefore overestimate the temperature. An additional issue is that the TBC translucency at conventional pyrometer wavelengths allows radiation from well below the TBC surface to reach the pyrometer so that surface-specific temperature measurements cannot be obtained. Two approaches have been pursued to overcome these difficulties. One successful approach

has been to develop long-wavelength (>10 μm) pyrometers that operate at wavelengths where the TBCs are opaque (to allow surface measurements) and the TBCs exhibit near-zero reflectance (to minimize interference of reflected radiation), but with the drawback of much lower signal and sensitivity than at shorter wavelengths.[3,4] Another successful approach has been to apply thermographic phosphors to the TBC surface to obtain emissivity-independent surface temperature measurements either by the temperature dependence of the fluorescence decay time or by the ratio of intensities of selected emission lines.[5,6]

One aspect of the potential for using thermographic phosphors for TBC temperature measurements that has not been well explored is to take advantage of the TBC translucency to place the phosphor not only at the surface, but at any depth where the temperature measurement is desired. The primary obstacle to depth-penetrating measurements is the attenuation of the excitation and emission intensities by the overlying TBC. In particular, YSZ-based TBCs are opaque to the ultraviolet (UV) excitation wavelengths that are normally used for surface temperature measurements. UV excitation of a thermographic phosphor layer has been previously used for subsurface temperature measurements; however, the depth penetration allowed by this approach is extremely limited.[7] In this paper, it is demonstrated that with an appropriately chosen excitation wavelength and detection configuration, sufficient phosphor emission is generated to achieve through-the-thickness temperature readings up to 1100 °C with the phosphor located beneath a 100 μm thick TBC. With further development, the strategic placement of luminescent species through the TBC could add embedded sensing functions to the TBC so that the photon-excited emission would pro-

Jeffrey I. Eldridge and Timothy J. Bencic, NASA Glenn Research Center, Cleveland, OH 44135; and Stephen W. Allison and David L. Beshears, Oak Ridge National Laboratory, Oak Ridge, TN 37831. Contact e-mail: Jeffrey.I.Eldridge@nasa.gov.